

Pyrolysis and oxidation of unsaturated C₂ and C₃ species

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Abstract

In this work we analyse and study several experimental data on pyrolysis, partial oxidation and combustion of C₂ and C₃ acetylenics as well as allene and ketene. These data, already presented in the literature, refer to turbulent flow reactors, jet stirred reactors (JSRs) and shock tube experiments and span wide ranges of concentration, pressure and temperature. In order to stress the importance of condensation reactions of unsaturated species some data of ethylene and propylene pyrolysis are also discussed. C₂ and C₃ unsaturated species are always present as important intermediates in combustion processes and their reactions play a crucial role in explaining the formation of aromatic and polyaromatic species in sooting flames. A detailed kinetic scheme able to describe the partial oxidation and the combustion of hydrocarbon mixtures up to commercial gasolines and liquid fuels is extended and more carefully validated on these sets of experimental data. The key reactions are discussed and compared with literature kinetic data. Moreover, this kinetic analysis is very useful for the study of ‘mild combustion’ in the intermediate temperature region where the flameless combustion seems to offer the great advantage of a reduced formation of toxic components such as nitric oxides, polyaromatics and soot. © 2000 Elsevier Science Inc. All rights reserved.

Keywords: Pyrolysis; Partial oxidation; Combustion

1. Introduction

Aim of this paper is to discuss the relevant kinetic features of the pyrolysis and oxidation of acetylene, methyl-acetylene (pC₃H₄) and allene (aC₃H₄) as well as ethylene, propylene and ketene. Unsaturated species and mainly acetylenics are always present as important intermediates in combustion processes, and their reactions play a crucial role in explaining the formation of aromatic and polyaromatic species possible precursors of particulate and soot. This kinetic analysis is also a critical step in order to properly recognise and define the recombination reactions of propargyl radicals. It also allows to understand the relative role of these resonantly stabilised radicals in comparison with the growing mechanism based on the H-abstraction on aromatic components and successive acetylene addition (HACA) [1,2]. The relative importance of and the competition between these two mechanisms clearly affect the formation of heavy species in the different sooting flames and the analysis of kinetically simpler experimental data

remains a preliminary step for the proper kinetic understanding of these systems.

For these reasons we analyse and review some pyrolysis data on ethylene and propylene carried out in plug flow reactor [3,4], acetylene oxidation data in jet stirred reactor (JSR) [5] and propyne and allene (propadiene) oxidation and ignition data not only in JSR and in shock tube experiments [6] but also in the Princeton turbulent flow reactor [7]. Oxidation of C₁–C₂ hydrocarbon mixtures in JSR are also discussed at intermediate temperatures [8].

All these data are obtained in mild temperature conditions. These conditions, which are easier to be handled from the experimental point of view are becoming also important at the industrial scale. The recover of waste heat by highly preheated combustion air requires the reduction of the high flame temperatures to avoid too elevated pollutant emissions (mainly nitric oxides). Energy saving has to be achieved by simultaneously increasing the exhaust gas recirculation and operating below the 1600–1700 K as local maximum temperature values.

Further examples are finally devoted to the analysis of acetylene [9] and ethylene [10] sooting flames. These data show the importance of these C₂ and C₃ unsaturated species and, as before mentioned, their role in

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explaining the formation of aromatic and polyaromatic species in sooting flamers.

A detailed kinetic scheme [11] is further validated and extended to better simulate new conditions and also to describe the behaviour of the two C_3H_4 different isomers. The sensitivity analysis and the reaction flux analysis allow to discuss the role of propargyl radicals. Furthermore the critical role on vinyl radical and ketene successive reactions appear a clear result of this kinetic study.

2. Kinetic model and experimental data

As already mentioned, several literature data have been studied and reviewed in order to better and further validate the kinetic model in the intermediate temperature region. During this analysis, the two different isomers of C_3H_4 , previously considered in terms of a single equivalent or 'lumped' component, have been taken into account and their reactions properly introduced. The overall kinetic scheme is a mechanistic model basically founded on a strongly modular and hierarchical structure, in which the simplest reaction sub-mechanisms are necessary to investigate the more complex ones. The overall mechanism, counting about three thousand reactions and two hundred species (molecules and radicals), includes both low and high temperature mechanisms used to model the hydrocarbon oxidation up to eight C atoms over wide operative ranges. The sub-scheme (HT9812) used in this work contains only the intermediate and high temperature mechanism, involves about 100 species and 1500 reactions and can be easily linked to the remaining part of the model. Because of space limitations, this kinetic model is not presented in this paper, but it can be directly requested to the authors.

The experimental data discussed and used for this extension of the kinetic model are the following:

- acetylene oxidation in JSR [5],
- propyne oxidation in Princeton turbulent flow reactor (PTFR) [7],
- allene and propyne oxidation in JSR [6],
- allene and propyne ignition [6],
- ethylene and propylene pyrolysis [3,4],
- C_1 and C_2 mixtures oxidation in JSR [8],
- ketene pyrolysis [12],
- ethylene [10] and acetylene [9] sooting flames.

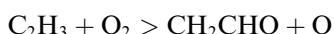
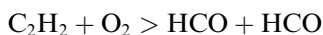
3. Acetylene oxidation in JSR

Tan et al. [5] presented four sets of experimental data on acetylene oxidation in the Orleans JSR at 1 and 10 atm and explored the effect of different stoichiometries.

Fig. 1(a) and (b) shows some comparisons between experimental data and model predictions in the four different conditions. It is possible to observe that the kinetic scheme well reproduces the experimental ignition

of the system in the temperature range from 800 to 1100 K.

A sensitivity analysis highlights the important role, at least, of the two following reactions:



respectively with the following rate parameters:

$$k = 0.6 \times 10^9 \exp(-22000/RT) \quad (1 \text{ mol}^{-1} \text{ s}^{-1}),$$

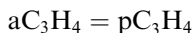
$$k = 0.8 \times 10^{12} T^{-0.78} \exp(-3135/RT) \quad (1 \text{ mol}^{-1} \text{ s}^{-1}).$$

Both these reactions act as radical chain initiation reactions (the second one as a degenerate branching path) and justify, respectively, the acetylene conversion at low temperatures (at 10 atm) and the proper location of the ignition inflection at atmospheric pressure.

Moreover the reaction path analysis allows to single out the critical role of ketene as a very relevant intermediate in acetylene oxidation. For this reason, model prediction of ketene pyrolysis will also be analysed later on.

4. Propyne oxidation in a turbulent flow reactor

Recently Davis et al. [7] have reported a detailed review on the kinetic studies specifically involving C_3H_4 isomers, both from an experimental and from a kinetic modelling point of view. The main goal of their study was to extend the validity of a kinetic scheme of propyne oxidation to cover wider operative conditions including also experimental data obtained from the PTFR. These data refer to three different experiments on propyne oxidation conducted on the PTFR in which the fuel to oxygen ratio was varied ($\Phi = 0.7, 1.0, 1.4$). These experiments give indications on allene formation and contribute to the tuning of kinetic parameters of the isomerization reaction



As already discussed by Davis et al. [7], this isomerization is not an elementary reaction. The reaction path via cyclo-propene (cC_3H_4) requires two internal 1–2 H-transfer steps. We did not include cC_3H_4 in the kinetic scheme and assumed, through a bimolecular reactions (with a third colliding partner), pressure dependent kinetic parameters:

$$k = 3.5 \times 10^{14} \exp(-59000/RT) \quad (1 \text{ mol}^{-1} \text{ s}^{-1}).$$

These rate expression is also close to the NIST suggested value [13] at 1 atm.

It is worthwhile observing that formally also the H addition on C_3H_4 should play a role in the isomerization of propyne and allene. As a matter of fact, the addition reaction of H radical to allene forms the 1-methyl-vinyl radical which can also decompose to propyne and hydrogen

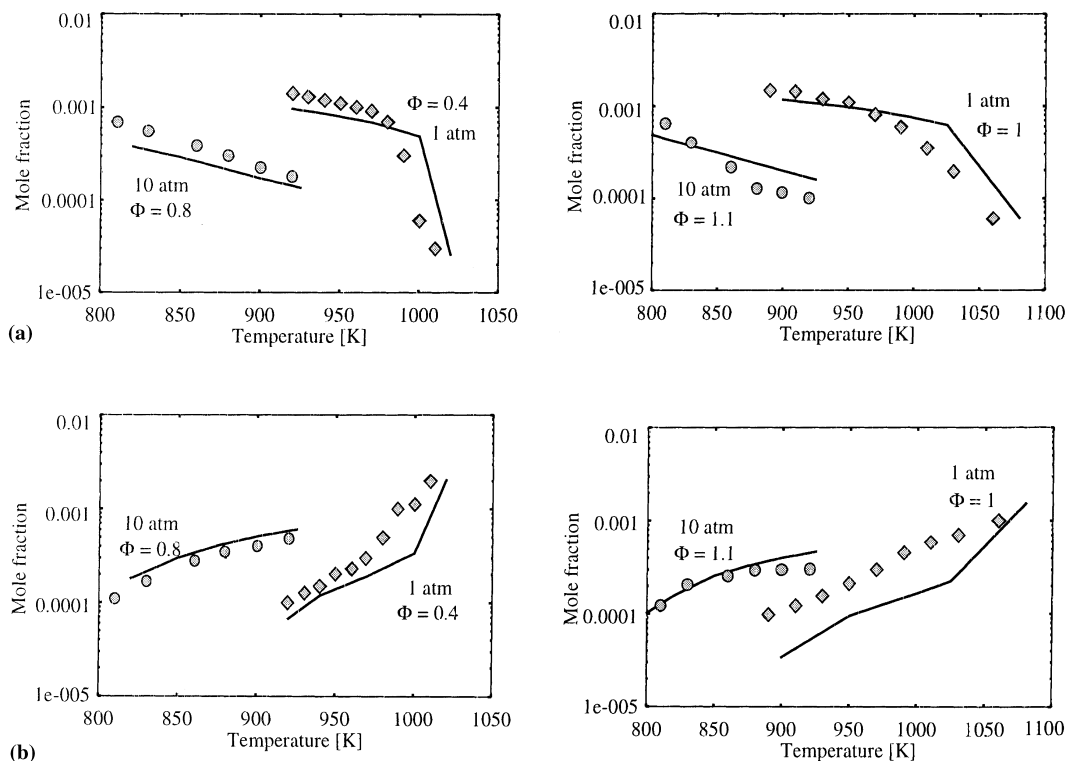
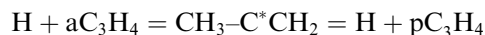
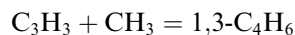


Fig. 1. Acetylene oxidation in JSR at 1 and 10 atm. Mole fraction of C_2H_2 (a) and CO_2 (b) vs temperature (K) [5].

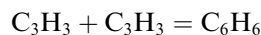
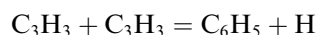
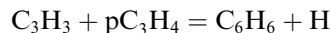


This path is much slower than the isomerization reaction previously reported.

Major species from propyne oxidation are also methane, acetylene, ethylene, ethane, butadiene and benzene. The formation of butadiene is justified by the recombination reaction of propargyl and methyl radicals:



while the formation of benzene, in these conditions, is mainly explained with the following reactions:



Some comparisons between model predictions and experimental data both in terms of conversion and of main products are reported in Fig. 2. The computed concentrations match quite well the experimental data at different propyne conversion, nevertheless the model slightly overpredicts the reactivity of the system.

5. Allene and propyne oxidation in JSR

The experimental data obtained by Dagaut et al. [14] on the allene and propyne oxidation in a JSR

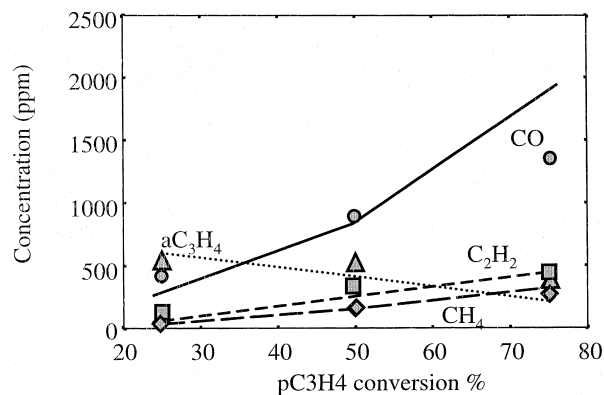


Fig. 2. Experimental [7] and predicted mole fractions of major species during propyne oxidation in PTFR with $\phi = 1$.

clearly indicate the difference between the two isomers and confirm the opportunity of a detailed kinetic modelling of both the two species. As a matter of an example Fig. 3 shows the higher acetylene yields obtained from propyne when compared to those from allene. The maximum is reached at about 900 K from propyne, while in the case of allene the C_2H_2 peak is about one half and is located at higher temperature. Due to space limitations only a few comparisons between predicted and experimental data are reported in Figs. 4 and 5 for both propyne and allene oxidation. The match is quite good both for the major products

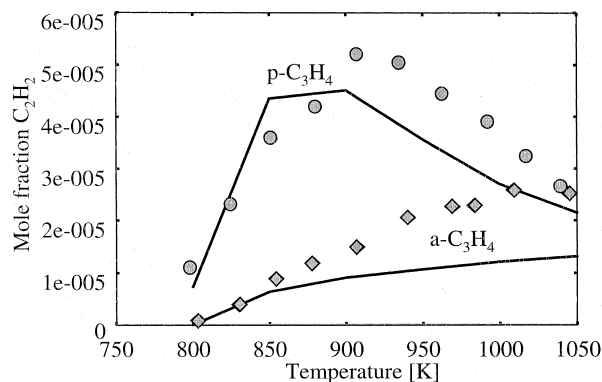


Fig. 3. Experimental [14] and predicted C_2H_2 mole fraction from propyne and allene stoichiometric oxidation in an isothermal JSTR at 10 atm and $\tau = 1.5$ s.

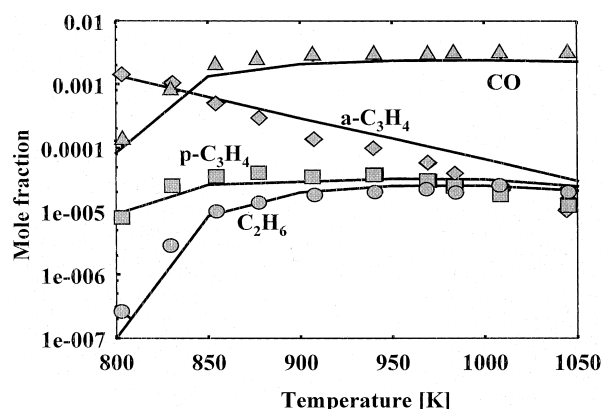


Fig. 4. Experimental [14] and predicted product mole fractions from allene stoichiometric oxidation in an isothermal JSTR at 10 atm and $\tau = 1.5$ s.

(CO and CO_2) and for minor species (C_2H_6). From Fig. 4 it is also possible to observe the effect of the isomerization reaction.

A more complete and detailed analysis of these data will be reported in a specific paper which is in progress.

6. Allene and propyne ignition

Curran et al. [6] report several experimental data on the ignition delay times of propyne and allene obtained in a shock tube device. These experiments span a wide range of conditions moving the temperature from 1100 to 2030 K, the pressure from 2 to 5 atm, the equivalence ratio from 0.5 to 2.0 and finally the fuel concentration from 0.5 to 2% (mole) in Argon.

The maximum in OH radical concentration has been used as a criterion for the determination of these ignition delay times. A first indication obtained from the experiments and well reproduced by the model is that, differently from the intermediates formation as

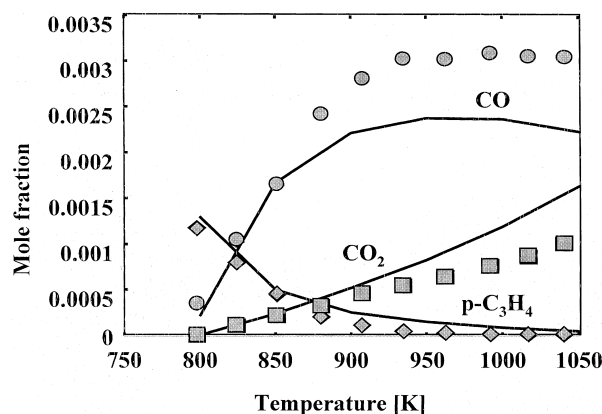


Fig. 5. Experimental [14] and predicted product mole fractions from propyne stoichiometric oxidation in an isothermal JSTR at 10 atm and $\tau = 1.5$ s.

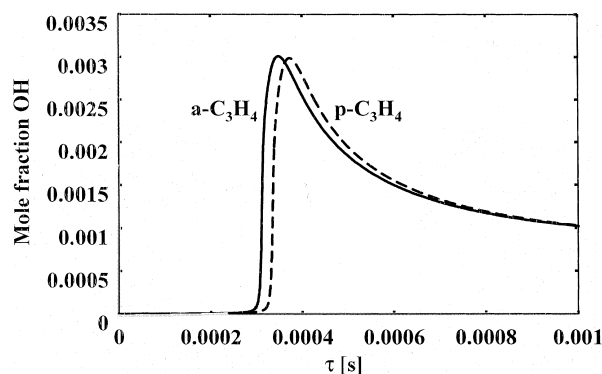


Fig. 6. Computed values of OH mole fractions during allene and propyne oxidation in shock tube. $T = 1390$ K, $P = 3.5$ atm, $\phi = 0.5$.

above reported, both the isomers are practically exhibiting the same ignition delays. This situation is well evident in Fig. 6 where OH radical concentration is reported versus the time for both fuels in the same conditions.

Figs. 7 and 8 show the comparisons of experimental data and model predictions respectively studying the influence of stoichiometry on propyne ignition and of dilution on allene. The agreement is quite good, the main effects are correctly reproduced not only qualitatively, but also quantitatively.

7. Ethylene and propylene pyrolysis

Due to space limitations, we are not reporting the full comparison between model predictions and the experimental data reported by Kunugi et al. [3,4]. These data, already discussed in a previous paper [15], show the importance of several cyclo-addition reactions of ethylene and acetylene on cyclopentadiene in the formation, via endomethylene species, of the first aromatic ring:

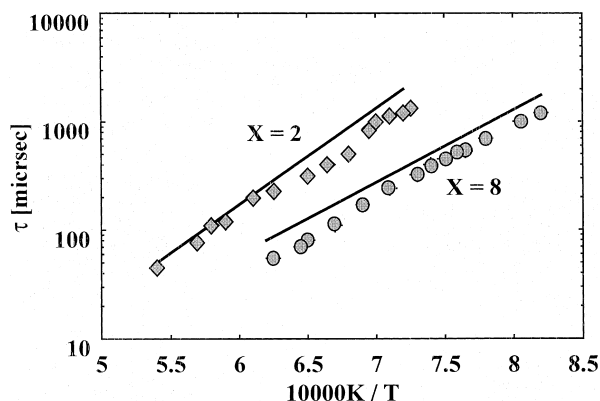


Fig. 7. Influence of dilution on propyne ignition in a shock tube; $P=3.5$ atm 1% propyne + $x\%$ of O_2 . Comparison between experimental [6] (symbols) and predicted (lines) data.

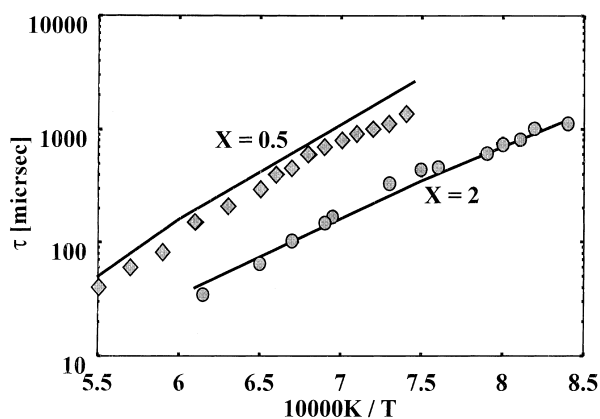
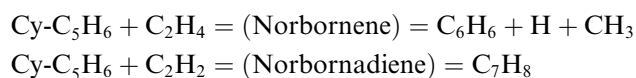


Fig. 8. Influence of dilution on allene ignition in a shock tube; $p=3.5$ atm $\phi=1$ x : allene percentage. Comparison between experimental [6] (symbols) and predicted (lines) data.



These reactions are important to justify the observed relevant selectivity in benzene. The first one is also a very important chain initiation reaction in the temperature range of 980–1127 K, due to the formation of two radicals.

As an example, Fig. 9 shows the comparison between experimental and predicted ethylene decomposition at two different temperatures. The presence of an induction period is explained by a dimerization of ethylene to form 1-butene, via a concerted four centre molecular reaction. The successive decomposition of 1-butene, forms methyl and allyl radicals and initiates the radical reaction chain. Fig. 10 shows the quite good agreement with the experimental data of predicted selectivity of selected species (methane, butadiene, cyclopentadiene and benzene). The same level of accuracy is obtained for the other species, like C_4 , which are extremely important in ethylene pyrolysis.

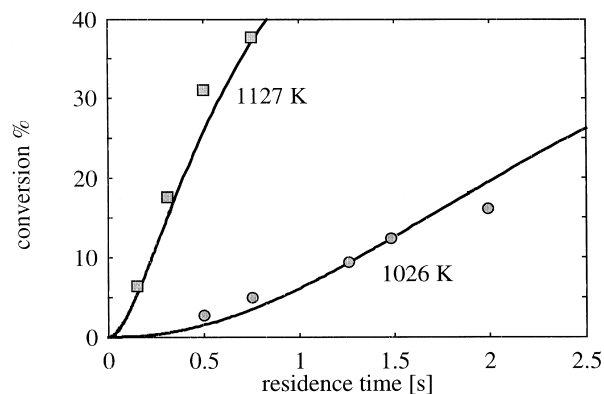


Fig. 9. Ethylene pyrolysis; comparison between conversion experimental [3] data (points) and model predictions (lines) at different temperatures.

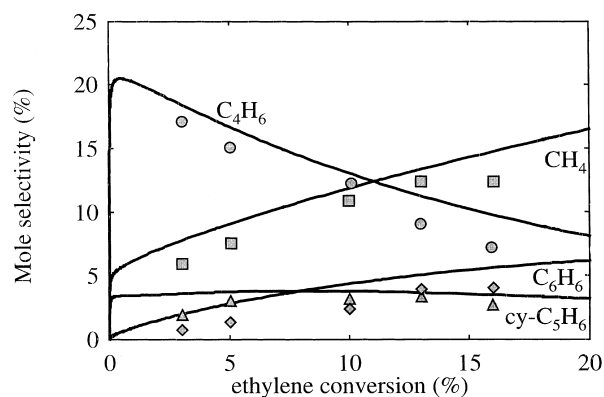
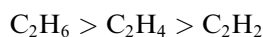


Fig. 10. Ethylene pyrolysis; mole selectivities vs. ethylene conversion at 1026 K. Symbols represent the experimental [3] measurements, and curves represent the model predictions for CH_4 , $cy-C_5H_6$, C_6H_6 .

8. C_1 and C_2 mixtures oxidation in JSR

Rota et al. [8] studied the oxidation of different mixtures of methane with C_2 species in an isothermal JSR very similar to the Orleans one. The different C_2 hydrocarbons are strongly influenced by their successive reactions:



therefore the behaviour of the oxidation of the four-hydrocarbon equimolar mixture necessarily shows an exotic behaviour in terms of their relative reactivities. An example of comparison between model predictions and experimental data is reported in Fig. 11. In this case an almost equimolar mixture of 500 ppm of CH_4 , C_2H_2 , C_2H_4 and C_2H_6 at $\phi=0.95$ diluted in N_2 is oxidised at 1 atm and about 0.1 s contact time. The model matches the CH_4 and C_2H_2 experimental data with a good accuracy, showing a higher reactivity of C_2H_6 at lower temperatures. Despite this fact, the initial maximum in ethylene is only partially reproduced. This

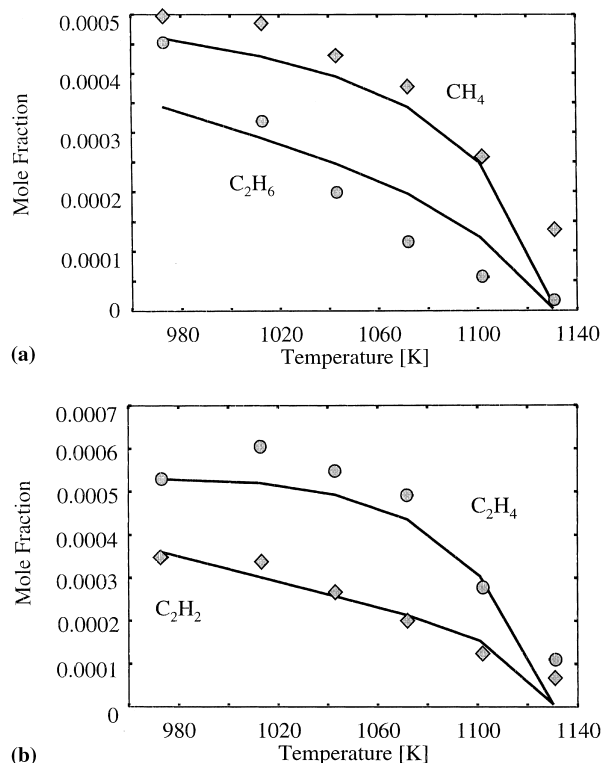


Fig. 11. Oxidation of a mixture of C₁ and C₂ hydrocarbons in JSR at 1 atm: comparison of model predictions (lines) with experimental profiles (symbols) [8].

flat behaviour is due to the initial formation of ethylene from ethane pyrolysis and oxidation.

9. Ketene pyrolysis

As already observed, ketene is quite difficultly detected and reported in the experimental investigations, even though it is an extremely important intermediate during C₂–C₃ oxidation. Further work from both the experimental and theoretical point of view should be addressed in a better characterisation and understanding of its oxidation and combustion paths. Hidaka et al. [12] studied the high temperature pyrolysis of ketene in shock waves at temperatures of 1100–1900 K and pressures of 1.2–2.7 atm.

They already discussed a detailed kinetic mechanism of 38 elementary reactions involving also acetylene, propyne and allene. Of course these pyrolysis reactions are hierarchically an essential part in the clarification of the complete oxidation mechanism. Main pyrolysis products detected by GC analysis were CO, H₂, CH₄, acetylene and ethylene. Ethane, propylene, allene, propyne butadiene and vinyl-acetylene were also detected only in smaller quantities. Model predictions are compared with the experimental yields in Table 1 (moles of products per moles of ketene fed) at 1500 K and 50% ketene conversion.

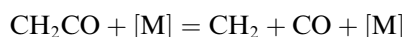
Table 1
Ketene pyrolysis^a

	Exp. ^b	Pred.
CO	100	99.4
CH ₄	9	5.9
C ₂ H ₂	12	9.3
C ₂ H ₄	25	35.7
C ₂ H ₆	0.5	0.4
aC ₃ H ₄	0.5	–
pC ₃ H ₄	1.4	0.1
C ₄ H ₄	0.4	0.2
Butadiene	0.2	0.1

^a Comparison between experimental and predicted moles of product per moles of ketene fed ($T = 1500$ K, Conversion = 50%).

^b Deduced from figures.

Ketene disappearance is due to the three body initiation reaction:

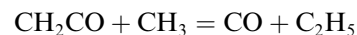


Fall-off parameters of this three body reaction are:

$$k_0 = 3.6 \times 10^{12} \exp(-59300/RT) \quad (\text{l mol}^{-1} \text{s}^{-1}),$$

$$k_\infty = 0.6 \times 10^{13} \exp(-76000/RT) \quad (\text{s}^{-1}).$$

Also important in ketene disappearance are the H and CH₃ radical addition reactions to ketene with the formation of CO and respectively CH₃ (via CH₃CO) and C₂H₅:



Rate parameters for these reactions are respectively:

$$k = 10^{10} \exp(-2000/RT) \quad (\text{l mol}^{-1} \text{s}^{-1})$$

$$k = 10^8 \exp(-2000/RT) \quad (\text{l mol}^{-1} \text{s}^{-1})$$

The initial formation of ethylene is justified by the dehydrogenation reaction of ethyl radical and by the recombination reactions of CH₂ and CH₃ radicals. Acetylene is mainly formed via the recombination of the resonantly stabilised HCCO radicals. Successive formation of acetylene is due to the dehydrogenation of ethylene while C₃ and heavier species are the result of radical additions on ethylene and acetylene.

10. Ethylene and acetylene sooting flames

As final examples, Figs. 12 and 13 show a few comparisons between model predictions and experimental data of ethylene [10] and acetylene [9] sooting flames. The agreement of the model with the experimental data is excellent in the ethylene flame, whereas in the acetylene flame the concentration of benzene is over predicted in the last part of the flame. A sensitivity analysis was performed on the benzene formation to show the relative importance of the HACA mechanism with respect to the propargyl radical recombination path in these

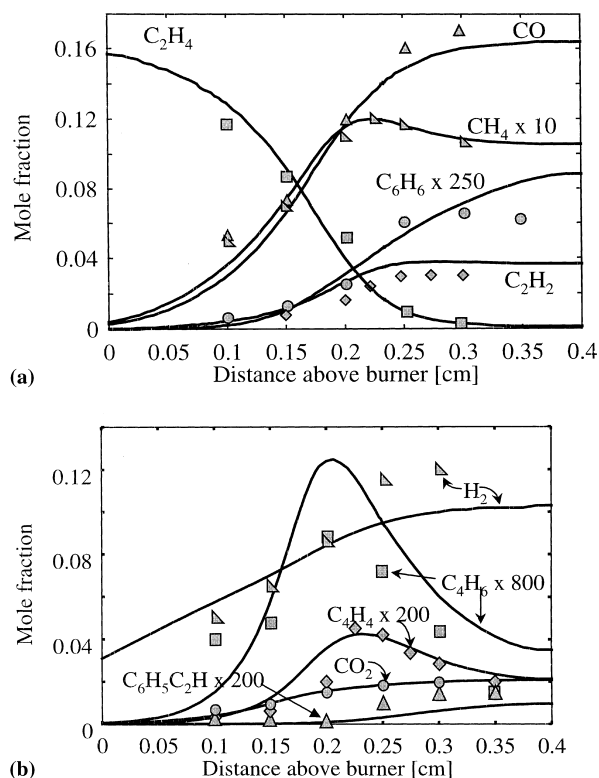


Fig. 12. Ethylene laminar flame [10]: comparison of model predictions with experimental profiles. Symbols represent the experimental measurements, curves represent the model predictions for H_2 , CO , CO_2 , CH_4 , C_2H_2 , C_2H_4 , C_4H_4 , C_4H_6 , C_6H_6 and phenyl-acetylene. Feed: C_2H_4 16.5%, O_2 17.9%, Ar 65.6%.

conditions. This analysis revealed that in the ethylene flame the role of the propargyl recombination radical mechanism is much more important than the HACA mechanism when the temperature is higher than 1400 K. The peak of the benzene production rate due to the HACA mechanism is almost 5 times less than that of the propargyl recombination path. Moreover, the ‘even way’ to benzene in these conditions is due to the ethylene rather than to the acetylene as highlighted in the flux analysis of Fig. 14, where the main benzene formation reactions close to the burner are reported.

In the acetylene flame the importance of the two different mechanisms is almost the same because the corresponding peaks of the benzene production rate are almost equal, but while the HACA path plays a dominant role in the first part of the flame, when the temperature is lower than 1300 K, the propargyl radical recombination mechanisms is the most important source of benzene at higher temperatures. It has to be noted that acetylene flame was carried out a very low pressure (20 Torr) and to correctly predict the low amount of benzene detected we reduced the propargyl recombinations at this very low pressure from 2×10^9 to 1×10^8 ($l \text{ mol}^{-1} \text{ s}^{-1}$), following Wang and Frenklach [2] indications.

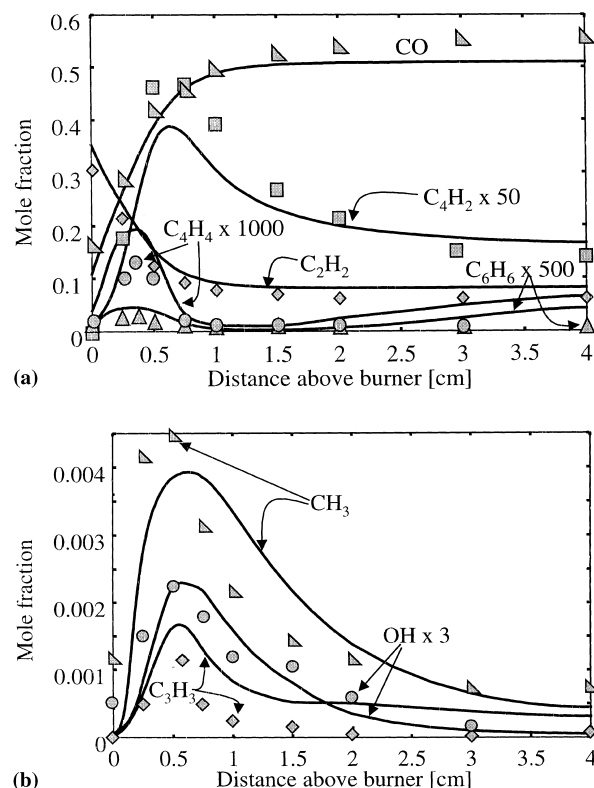


Fig. 13. Acetylene laminar flame [9]: comparison of model predictions with experimental profiles. Symbols represent the experimental measurements, and curves represent the model predictions for molecules (panel a). CO , C_2H_2 , C_2H_4 , C_4H_4 , C_6H_6 and radicals (panel b). Feed: C_2H_2 46.5%, O_2 48.5%, Ar 5%.

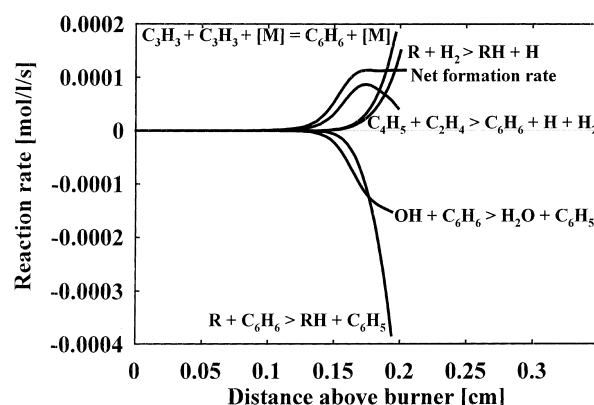


Fig. 14. Ethylene flame: reaction flux analysis of benzene formation close to the burner.

11. Conclusion

The kinetic analysis of these sets of experimental data allowed a further and useful validation of the overall reaction scheme of hydrocarbon oxidation and combustion to cover also new operating conditions.

The pyrolysis and oxidation reactions of these unsaturated C_2 and C_3 species, always present as important

intermediates in combustion processes, have a critical role in explaining the formation of aromatic and polycyclic aromatic species in sooting flames and also show the critical role on successive oxidation reactions of ketene. To this purpose there is a clear need of new experimental data of ketene oxidation in order to better characterise its successive oxidation and decomposition fates.

Mainly the data of C_2H_4 and C_2H_2 rich premixed laminar flames show the importance of the competition between the two alternative paths to benzene formation (propargyl radical recombination and HACA or acetylene additions). The $(C_4 + C_2)$ cyclo-addition mechanism with the successive ethylene/acetylene addition on cyclopentadiene is more important at lower temperatures, i.e., in the first part of the flames (as well as in the ethylene and propylene pyrolysis).

Moreover, this kinetic study is also a very useful step for a further validation of the overall kinetic scheme in the intermediate temperature region, the so called 'mild combustion' conditions, where this 'flameless combustion' seems to offer the great advantage of a reduced formation of toxic components such as nitric oxides, polyaromatics and soot.

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